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(54) Additive for aqueous quenching by immersion of aluminium-base alloys

(57) An agent for aqueous quenching of components of aluminium alloys, that have been previously raised to a temperature of at least 430°C comprises, per litre of water, from 5 to 35 g and preferably from 6 to 20 g of polyvinyl pyrrolidone and from 50 to 250 g of an additive that causes reversible precipitation of polyvinyl pyrrolidone at the surface of the components at the moment when they are introduced into the quenching agent.

The most effective additive is sodium chloride, in a concentration of from 100 to 250 g/l.

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SPECIFICATION

Additive for aqueous quenching by immersion of aluminium-base alloys

The present invention concerns an additive for aqueous quenching agents for aluminium-base alloys.

In order to achieve their optimum properties most aluminium-base alloys having high mechanical characteristics must be subjected to a series of thermal and mechanical treatments and in particular a quenching operation, which generally follows formation of a solid solution, at an elevated temperature usually at least equal to 430°C.

At the present time, the quenching operation is carried out using cold, warm or boiling water, depending on the particular circumstances involved, and the results obtained are not always the best possible compromise between the mechanical characteristics required, e.g. the dimensional stability of the components and their resistance to stress corrosion.

It is known that quenching ferrous alloys (carbon steels or alloy steels), which is often carried out in special oils, can also be performed in aqueous agents containing water-soluble organic polymers as additives.

Thus, in 1960, in a marketing brochure, Wyandotte Chemical Co. recommended using polyoxyalkylene glycols as an additive for quenching agents. The substance, which was identified by the registered trade mark Pluracol V 10, had a molecular weight of from 25000 to 35000.

In 'Metals Handbook', it is stated that the addition of 0.01% of polyvinyl alcohol to quenching water substantially increases the rate of cooling during the calefaction phase.

French Patent FR-A-1 384 244 (equivalent to US-A-3 220 893) to Union Carbide Co. describes aqueous agents based on polyalkylene glycols, with the addition of anti-corrosion agents such as nitrite or borates.

French Patent FR-A-1 525 603 to B.A.S.F., A.G. discloses the addition of a water-soluble polymer containing (—CO-NH—) groups, in a proportion of from 0.1 to 1% by weight.

German Patent Application DE-OS No. 23 49 225 provides for the addition of 0.4 to 10% by weight of a polyacrylic acid salt to water.

French Patent FR-A-2 316 336 (equivalent to US-A-4 087 290) to Houghton & Co. states that the additive can also be a water-soluble salt of polyacrylic acid.

Finally US Patent No. 3 902 929 assigned to Park Chemical Company proposes the use of polyvinyl pyrrolidone of a mean molecular weight of from 5000 to 400000, with the addition of nitrite and/or borax ($Na_2B_4O_7$) as an anti-corrosion agent, together with a biocide such as paraformaldehyde.

However, none of the above-identified documents provides or suggests the possibility of using such additives for the aqueous quenching of aluminium-base alloys.

It is known that the operation of quenching aluminium alloys involves structural phenomena that are different from those involved in quenching steels, and it is not possible to simply transfer the procedure from one situation to the other.

Efforts have therefore been made to develop a specific aqueous quenching agent for quenching aluminium alloys that gives the best possible compromise between the mechanical tensile strength characteristics and dimensional stability with respect to quenching of thin or precision-die-cast components, and between the mechanical tensile strength characteristics and the residual stresses resulting from quenching of thick components. In dealing with thin or precision-die-cast components an essential criterion is isothermy of the surfaces and the possibility of reproducing the cooling effects; when dealing with thick components, an essential criterion is the attainment of accelerated reproducible cooling rates that permit of rapid quenching of the alloys in the critical quenching range (400 to 250°C) without causing excessive softening of the skin or surface layer of the metal, in particular at temperatures between 500 and 400°C. Such compromises are achieved by introducing suitably selected additives into the quenching water.

The present invention provides an aqueous quenching agent for quenching components of aluminium alloys, comprising, per litre of water, from 5 to 35 g. and preferably from 6 to 20 g. of polyvinyl pyrrolidone together with an additive that, in the hot condition, causes instantaneous reversible precipitation of the polyvinyl pyrrolidone on the quenched component. Use was made of the polyvinyl pyrrolidone produced by Badische Anilin and Soda Fabrik (BASF) under the reference "K 90", its mean molecular weight being about 700000 and in any case higher than 400000, while it may attain 1000000.

The additive may be a water-soluble organic substance or a mineral salt that is soluble in water and in aqueous solutions of polyvinyl pyrrolidone. However, sodium chloride has been found to be best suited to carrying the invention into effect. The additive may be introduced in a proportion of from 5 to 250 g/l and, when the additive is NaCl, 100 to 250 g/l and preferably 150 to 200 g/l.

It was found that quenching a cylindrical testpiece of aluminium alloy by immersing it in the quenching agent according to the present invention had the following effects:

(1) With concentrations of polyvinyl pyrrolidone (referred to in abbreviated form hereinafter as "PVP") ranging from 6 to 20 g/l of water and with the addition of sodium cloride, the cooling effect achieved was (a) of uniformly retarded type with mean cooling rates that decrease in proportion to increases in the concentration of NaCl (up to 100 g/l) and (b) of uniformly accelerated type (up to 250°C) with rising mean cooling rates, when the proportion of NaCl rises from 150 g/l to 250 g/l. In that case, the cooling rate is slightly higher (between 500 and 400°C) or lower (in the critical quenching range of 400 to 250°C) than that achieved by immersion in water at 60°C, in a non-agitated condition.

Therefore, from 150 to 200 g/l of NaCl should be added to the PVP solutions in order to achieve cooling of the accelerated type, which is advantageous in respect of the compromise between mechanical

properties and quenching deformation.

(2) When the component to be quenched is immersed, it is found that there is progressive and reversible precipitation of a thick insulating layer of PVP at the surface of the testpiece (beginning at the bottom), followed by rapid, complete re-dissolution of that layer at the end of the cooling phase (at about 100 to 150°C) if the proportions of additives dissolved remain lower than or equal to 20 g/l of PVP and 250 g/l of NaCl.

(3) Agitation permits of an increase in the cooling rates of solutions containing 100 g/l of NaCl but it does not cause a significant acceleration in the cooling rate in solutions containing 150 to 200 g/l of NaCl, which are therefore substantially insensitive to differences in agitation. On the other hand, it promotes the simultaneous precipitation of the PVP over the entire surface of the testpiece, which is *a priori* also favourable to reproducibility of the treatments and to minimizing residual stresses or deformation on components of large dimensions.

(4) With proportions of NaCl of 150 to 200 g/l, the rate of cooling is independent of the PVP content (between 6 and 20 g/l) and the state of surface oxidation of the metal. In addition, in contrast to cold water or *a fortiori* hot water (60°C), the solutions containing PVP in a proportion of 12.5 g/l + NaCl in proportions of from 150 to 200 g/l, which are prepared under the same conditions from the same batch of basic substances, give reproducible cooling effects that are substantially insensitive to the temperature of the solution at from 15 to 25°C.

The following Tables set out the results of quenching tests carried out on a split tube of AU4G (2017) and on plate made of 7075, which show the attraction afforded by solutions of PVP + salt.

The test conditions are set out below:

Optimum concentrations: aqueous solution of PVP in a proportion of from 5 to 20 g/l, preferably 10 to 15 g/l, with the addition of 100 to 250 g/l and preferably from 120 to 200 g/l of NaCl.

EXAMPLE No. 1

This test, which seeks to evaluate deformation due to the quenching operation, was carried out on a tube made of AU4G (2017), with a length of 230 mm, Ø of 60 mm and a thickness of 2.5 mm, split along a generatrix with 25 mm between the lips so defined.

The tube was subjected to a solid-solution treatment lasting for 15 minutes at a temperature of 480°C.

Batches of 4 tubes were treated. They had been quenched by vertical immersion in a 100-litre tank without agitation. The amount by which the lips had come together (−) or moved apart (+) was then measured, at 5 points at spacings of 40 mm, and the average of the 5 measurements over each of the 4 tubes was used.

Comparative tests were also carried out, using water at 20°C and at 60°C, and air:

Fluid	Cooling rate in °/s	Deformation of tubes No 1	2	4	3	Average	Mini/Maxi
PVP 12.5 g/l + 150 g NaCl	250	+0.11	0.08	0.13	0.09	0.10	0.14
PVP 12.5 g/l + 200 g NaCl	350	+0.18	0.10	0.17	0.08	0.14	+0.14/−0.22
Air	1.1	+0.14	+0.08	+0.10	+ 0.06	+0.095	0.02/0.18
Water 20°C	600	+0.58	+0.50	+0.30	+ 0.61	+0.50	0.22/0.92
Water 60°C	200	+0.26	+0.05	−0.03	+ 0.02	+0.11	−0.09/0.30

EXAMPLE No. 2

Measurements were then made in respect of the influence of the quenching operation on the mechanical characteristics and deformation of metal plates made of 7075 (AZ8GU) measuring 400 x 400 x 8 mm, which were quenched by rapid vertical immersion in a 200-litre tank. The plates had been previously subjected to a solid-solution treatment for a period of 4 hours at a temperature of 480°C.

Comparative tests were carried out by quenching with water at 20°C and at 60°C. The results are as follows:

Quenching fluid	Elastic limit Rp 0.2, MPa	Breaking stress Rm, MPa	Elongation A %	Deformation in mm "Sag"	"Tile-type"	Cooling rate °C/s
PVP at 12.5 g/l + 150 g NaCl	487	563	15.5	0.0	0.0	80
PVP at 12.5 g/l + 200 g NaCl	487	563	16.1	0.0	0.0	100
Water 20°C	498	568	11.6	1.5	1.5	200
Water 60°C	486	559	12.5	5	7	60/110

"Sag" is longitudinal bowing; "Tile-type" is transverse bowing.

It appears therefore that this quenching agent considerably improves the compromise in regard to mechanical strength, deformation on quenching and residual stresses. It gives results markedly better and more reproducible than those obtained using hot water for quenching.

It will be appreciated that the components of aluminium alloys quenched in the above-indicated agent containing NaCl must be subjected to a final rinsing with water in order to prevent any risk of subsequent corrosion, however slight.

Although other salts such as borax ($Na_2B_4O_7$) (up to 50 g/l) and sodium sulphate (to 80 g/l) give interesting results, only sodium chloride was such as to ensure both stability of the quenching agent (it does not cause irreversible precipitation of PVP) and an optimum compromise between the various characteristics involved.

CLAIMS

1. An aqueous quenching agent based on polyvinyl pyrrolidone for quenching components of aluminium-base alloy that have been previously raised to a temperature that is at least equal to 430°C and comprising, per litre of water, from 5 to 35 of polyvinyl pyrrolidone and from 50 to 250 g of an additive causing reversible precipitation of polyvinyl pyrrolidone at the surface of the components at the moment when they are introduced into the quenching agent.

2. An aqueous quenching agent as claimed in Claim 1 containing from 8 to 20 g/l of polyvinyl pyrrolidone.

3. An aqueous quenching agent as claimed in Claim 1 or 2, in which the polyvinyl pyrrolidone has a mean molecular weight at least equal to 400000.

4. An aqueous quenching agent as claimed in Claim 3, in which the polyvinyl pyrrolidone has a mean molecular weight that attains 1000000.

5. An aqueous quenching agent as claimed in any preceding claim, in which the additive is sodium chloride in a concentration of from 100 and 250 g/l.

6. An aqueous quenching agent as claimed in Claim 5, in which the sodium chloride concentration is 150 to 250 g/l.

7. An aqueous quenching agent as claimed in Claim 1 substantially as hereinbefore described.

8. Aluminium-base-alloy components that have been raised to a temperature of 430°C and subsequently quenched using an aqueous quenching agent as claimed in any one of the preceding claims.

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